PARTICIPATION OF SULFUR COMPOUNDS IN

VINYL AND RELATED POLYMERIZATION

by

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A wide variety of sulfur compounds is known to participate in vinyl and related polymerization. Some of them function as initiators or as a part of an initiator system, some as modifiers, chain-terminating agents or inhibitors, and some as monomers or comonomers or as active solvents in the polymerization process. The object of the present article [paper] is to review the area of vinyl and related polymerization involving sulfur-bearing initiator systems, modifiers or chain-transfer agents and solvents in general, putting emphasis on recent reports in this field in particular. Description of the polymerization and copolymerization of a host of sulfur-bearing monomers is beyond the scope of the present review, excepting, of course, for some special cases of particular interest and peculiarity.

Peroxy Compounds

Peroxy-disulfate or persulfate ion, $S_2O_8^=$ is one of the widely used initiators in aqueous emulsion polymerization. It decomposes unimolecularly[1,2] in aqueous media producing two sulfate ion radicals SO_4^-. The radical-forming reaction arises from the simple homolytic
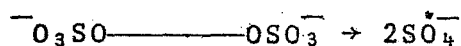
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cleavage of the peroxy bond:

$$^-O_3SO\text{------}OSO_3^- \rightarrow 2S\overset{\bullet}{O_4}{}^-$$

The sulfate ion radicals formed are efficient imitiators of polymeriza-
tion. When S^{35}-labeled persulfate was used[3,4] in the emulsion poly-
merization of styrene, essentially all the persulfate decomposed
appeared in the polymer as sulfate end-groups. In the absence of an
organic substrate, the sulfate ion radicals in aqueous solution are
believed to react further as follows:

$$S\overset{\bullet}{O_4}{}^- + H_2O \rightarrow HSO_4^- + \overset{\bullet}{O}H; \quad 2\overset{\bullet}{O}H \rightarrow H_2O + \tfrac{1}{2}O_2$$
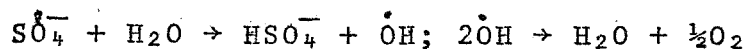
Recent reports[5] based on end-group analysis of aqueous persulfate
initiated poly (methyl methacrylate) and polystyrene indicate that
both sulfate ion radicals and hydroxyl radicals take part in the initi-
ation process during polymerization in neutral media, and that the
sulfate ion radicals are the preferred initiating radicals in alkaline
conditions, while initiation is almost exclusively by $\overset{\bullet}{O}H$ radicals in
strongly acidic media. It appears that in acidic conditions, the
anionic sulfate radicals rapidly react with the protonated water mole-
cules to from hydroxyl radicals:

$$S\overset{\bullet}{O_4}{}^- + H_3\overset{+}{O} \rightarrow H_2SO_4 + \overset{\bullet}{O}H$$

SenGupta and Palit[6] studied the persulfate-initiated polymeriza-
tion of methyl methacrylate in ethylene glycol solution and observed

that in this system at 80°c, the rate of polymerization (and also the degree of polymerization) was much higher than that in a benzoyl peroxide-initiated system under similar conditions. Okamura and Motomyama[7], however, did not report such great differences in the rate and degree of polymerization of methyl methacrylate and vinyl acetate in a homogeneous system (using a dioxane-water or aytic acid-water mixture as solvent) using separately benzoyl peroxide, azobisisobutyronitrile and ammonium persulfate as the initiator. Kiuchi and Watanabe[8] observed lower values of k_t/k_p^{2} (where k_t and k_p are the rate constants of termination and propagation respectively) in the persulfate-initiated polymerization of acrylonitrile in dimethyl sulfoxide solution as compared to that in azobisisobutyronitrile-initiated polymerization in the same solvent. These observations[6-8] have been interpreted, at least in part, in terms of a reduced rate of termination in the persulfate-initiated systems. This is due to mutual repulsion of the growing chains caused by the presence of negatively charged end groups in them arising from initiation by sulfate ion radicals.

While studying the persulfate-initiated polymerization of acrylonitrile in dimethyl sulfoxide solution, Kitagawa[9] observed that the rate of polymerization was directly proportional to the concentration of the solvent. This was explained by considering the following reaction between the persulfate ion and the sulfoxide molecule:

$$S_2O_8^{=} + 2(CH_3-\overset{O}{\underset{}{S}}-CH_3) \rightarrow 2SO_4^{=} + 2(CH_3-\overset{O}{\underset{}{S}}-CH_3)^{+}$$
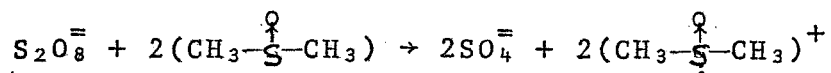
Sulfonyl peroxides have also been reported[10] to decompose into radicals at low temperatures. Bis-phenyl sulfonyl peroxide prepared from benzene sulfonyl chloride and sodium peroxide (8-10% yield) has been reported[11] to polymerize methyl methacrylate easily at 25°c while benzoyl peroxide fails to give any polymer under similar conditions. The sulfonyl peroxide, $C_6H_5SO_2-O-O-SO_2C_6H_5$, decomposes into radicals by scission of the 0-0 bond and in benzene solution in the absence of any other substrates, the following reaction is believed to take place:

$$C_6H_5-SO_2-O-O-SO_2-C_6H_5 \xrightarrow{\quad C_6H_5 \quad} C_6H_5-SO_2-O-C_6H_5 + C_6H_5-SO_2-OH$$
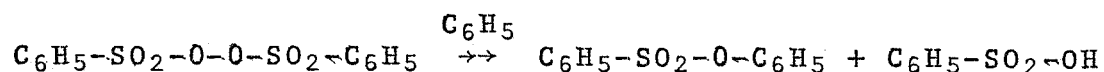
## Diazothioether and sulfonyl azide compounds

Diazothioethers (R-N=N-S-R') are known[12] to be useful initiators and modifiers in emulsion polymerization. During their thermal decomposition, an active aromatic radical $R^\bullet$ and a less active mercapto radical $R'S^\bullet$ are generated simultaneously:

$$R-N=N-S-R' \rightarrow R^\bullet + N_2 + R'S^\bullet$$
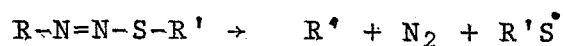
The activity of the diazothioethers as initiators and retarders depends[13] on the substituents R and R'.

Another group of interesting polymerization initiators is the sulfonyl azides. The use of benzene sulfonyl azide $C_6H_5-SO_2-N_3$ in radical reactions is known (radicals being generated by the unimmolecular decomposition of the sulfonyl azide molecules) and the initiation of polymerization of methyl acrylate and acrylonitrile in presence of
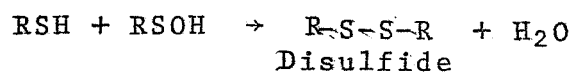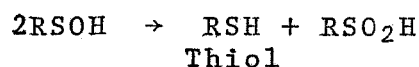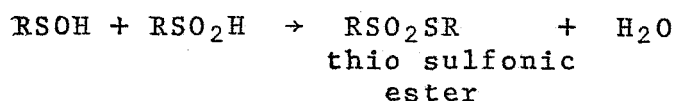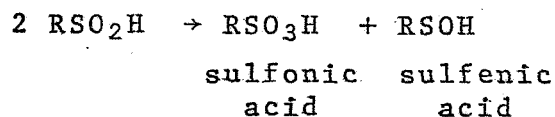
this compound has been reported.[14] The benzene sulfonimido diradical is produced along with nitrogen during the decomposition of benzene sulfonyl azide.

$$C_6H_5SO_2N_3 \rightarrow C_6H_5-SO_2-\overset{.}{N}. + N_2$$
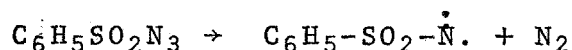
Investigations on the decomposition of a number of p-substituted aryl sulfonyl azides and polymerization of some vinyl monomers initiated by these azides in the temperature range of 110-130°c have recently been reported[15,16]. The sulfonyl azides easily initiate polymerization of acrylonitrile, styrene and methyl methacrylate at 30°c under ultraviolet radiation[15]. In the thermal polymerization of acrylonitrile, the rate of polymerization has been shown[15] to be proportional to the 0.5 power of the initial concentration of the aryl sulfonyl azides. The overall activation energy for the decomposition of benzene sulfonyl azide has been reported[16] to be 36.4 kcal/mole.

Organic Sulfoxy Compounds

Sulfinic acids, RSO_2H, which are organic acids of tetravalent sulfur, are known for their tendency to decompose. The decomposition reactions may be written as follows:

$$2 \ RSO_2H \rightarrow \underset{\substack{\text{sulfonic} \\ \text{acid}}}{RSO_3H} + \underset{\substack{\text{sulfenic} \\ \text{acid}}}{RSOH}$$

$$RSOH + RSO_2H \rightarrow \underset{\substack{\text{thio sulfonic} \\ \text{ester}}}{RSO_2SR} + H_2O$$

$$2RSOH \rightarrow \underset{\text{Thiol}}{RSH} + RSO_2H$$

$$RSH + RSOH \rightarrow \underset{\text{Disulfide}}{R-S-S-R} + H_2O$$

Hagger[17] first reported the use of sulfinic acids as excellent low-temperature initiators for the emulsion and bulk polymerization of ethylenic and vinyl monomers. Polymerization of methyl methacrylate starts instantaneously with no inhibition period, even in presence of normal stabilizers. Hydroquinone enhances the catalytic action of the sulfinic acids[17,18] while quinone and oxygen act as an inhibitor and a retarder, respectively, during polymerization. Overberger and Godfrey[19] investigated the sulfinic acid - initiated polymerization of methyl methacrylate dilatometrically at 30 $^{\circ}$C, using specially-purified materials and high-vacuum systems. They observed that the reaction order with respect to the initiator concentration was between 1 and 1.5 instead of 0.5 as previously reported[17], showing that the order of initiation was between 2 and 3. p-Toluene sulfonic acid, benzoyl peroxide and di-n-butylamine hydrochloride were reported to accelerate polymerization, but the rate was unaffected in the presence of Fe^{3+} ion. The rate of polymerization initiated by benzene (or toluene) sulfinic acid as observed by Overberger and Godfrey were much slower than those reported by other workers who found the rates to be 0.5 order in sulfinic acid. On the basis of their experiments, Overberger and Godfrey concluded that the kinetic discrepancies in earlier reports (0.5 order dependence of rate on sulfinic acid concentration) could be explained by assuming the presence of adventitious impurities which were oxidizing or reducing agents and which formed redox systems capable of initiating polymerization at a rate sufficient to mask the rate of polymerization

due to sulfinic acid alone. Interestingly an increase in rate of polymerization on dilution with benezene was reported[19] in the sulfinic acid-initiated polymerization of methyl methacrylate. This effect was probably due to enhanced association of the sulfinic acid molecules in the benzene-diluted system.

Later Iring et.al.[20] also made dilatometric studies of styrene polymerization using p-toluene sulfinic acid as the initiator at 45-65°C. They found, however, a square-root dependence of rate on initiator concentration. When benzoyl peroxide was also present in the system, the rate was proportional to the square root of the peroxide concentration and the rate and degree of polymerization were unaffected by variation in the sulfinic acid concentration.

Imoto and Ukida[21] reported an acceleration in the rate of vinyl acetate polymerization using the mixed catalyst system of azobisisobutyronitrile and p-chloro benzene sulfinic acid, particularly when the molar ratio of the sulfinic acid to the azonitrile was less than unity. By polarographic study of the reaction between the sulfinic acid and the azonitrile, the mixed-catalyst effect was explained by a direct reaction between the two compounds.

There are reports in the patent literature[22-24] of the use of a variety of sulfoxy compounds as accelerators of polymerization of olefin, diolefin or vinyl compounds. In a recent report[24], use of compounds of the formula RSO_2X, $RSOX$, RSX and S_nX_2 (where R is an alkyl, cyclo-alkyl or aryl group or a halogen derivative thereof and X represents a halogen atom, and $n = 1$ or 2) as catalysts for the polymerization and

copolymerization of 1-olefins and polyenes has been mentioned. Amino-
alkyl sulfone compounds of the general formula RSO CHR'X (where R is a
hydrocarbon group, R' is H or a hydrocarbon group and X is an amino
or substituted amino group) have also been used[23] as efficient acceler-
ators of olefin, diolefin and vinyl compounds at a relatively low
temperature (35°c).

Elemental Sulfur

It is appropriate to consider the role of elemental sulfur in
polymerization at this stage, before opéning the discussion on the sim-
ilar role of organic sulfides and polysulfides. Elemental sulfur is
known to exist as a stable cyclic S_8 molecule from room temperature to
some what above its melting point. With increase in the temperature
of molten sulfur, the liquid darkens and increases rapidly in viscosity,
which reaches a maximum at around 185°c. This phenomenon has been
explained[25] on the basis of an equilibrium between S_8 rings and long
chains of sulfur, which attain a maximum length at the point of maxi-
mum viscosity. Homolytic cleavage of the S_8 rings at elevated tempera-
tures yields a diradical which then initiates a free radical polyeri-
zation and in fact, physical measurements and calculations indicate
that the long sulfur chains are diradicals.

$$S_8$$

$$\cdot S\text{-}S_6\text{-}S. \quad \rightleftharpoons \quad \cdot S\text{-}S_{14}\text{-}S. \quad \text{etc.}$$
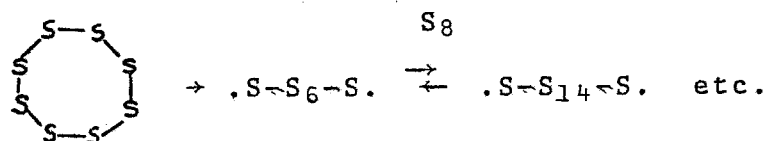
One of the direct evidences of the participation of elemental
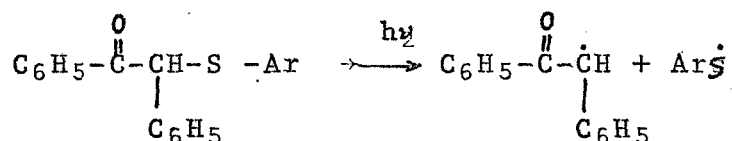sulfur in free-radical reactions is its effectiveness as an inhibitor

in vinyl polymerization[26]. Vinyl acetate radicals attack sulfur about

470 times as fast as they add monomer and the resulting products

(supposedly polysulfides. M-S$_8$M., .M-S$_6$M.., etc.) in turn also behave

as inhibitors, being attacked by radicals only somewhat less readily[27].

While studying the inhibition of thermal polymerization of styrene,

Bartlett and Trifan[28] observed that the initial product was a low-mole-

cular-weight copolymer containing approximately eight sulfur units per

styrene unit. On further heating, the sulfur content in the copolymer

decreased, probably by chain transfer with the polysulfide groups

present. Gladisher and Leplyanin[29] also reported évidence of copoly-

merization of sulfur and methyl methacrylate during postpolymerization

in the photoinitiated polymerization of methyl methacrylate in the

presence of sulfur inhibitor.

Organic sulfides

Quite a large number of organic sulfides, disulfides and poly-

sulfides have been studied as possible initiators of vinyl polymeri-

zation. Britenbach and Schindler[30] reported that at 70°c, dibenzoyl

disulfide, $C_6H_5\overset{O}{\overset{\|}{C}}-S-S-\overset{O}{\overset{\|}{C}}C_6H_5$, decompose slowly to give free radicals

which induce vinyl polymerization. Frank et.al.[31] also reported the

ability of dibenzoyl disulfide to initiate vinyl polymerization by a

radical mechanism. Otsu and coworkers, however, described this disulfide

as ineffective as a thermal initiator (60-120°c) of polymerization.[32,33]

Many other aromatic disulfides such as diphenyl, dibenzyl, dithiobenzyl,

dinitro-diphenyl, dibenzothiazyl and dialkyl xanthogene disulfide, were

also reported[32,33] to be ineffective as thermal initiators of polymeri-

zation but some of them were found[32,34-36] to act as retarders of poly-

merization. Ferrington and Totoloky, however, reported[36] that dephenyl

disulfide exhibited a combination of initiating and retarding ability

at 100°c. Most of the organic disulfides mentioned above and certain

monosulfides are effective poloinitiators of vinyl polymerization[32,33].

Petropoulos[37] studied the kinetics of photopolymerization of

tetraethylene glycol dimethacrylate in the bulk with the use of a number

of desyl aryl sulfides, $C_6H_5-\overset{O}{\overset{\|}{C}}-CH(C_6H_5)-S-Ar$ (where Ar is an aro-

matic group), as photoinitiators at 25°c. The rate of polymerization

was found to be proportional to the square root of the initiator concen-

tration. The desyl aryl sulfides are believed to decompose into radi-

cals according to the following mechanism:

$$C_6H_5-\overset{O}{\overset{\|}{C}}-\underset{\underset{C_6H_5}{|}}{CH}-S-Ar \quad\xrightarrow{h\nu}\quad C_6H_5-\overset{O}{\overset{\|}{C}}-\underset{\underset{C_6H_5}{|}}{\overset{\cdot}{C}H} + Ar\overset{\cdot}{S}$$

It was indicated from polymerization experiments that resonance stabi-

lization of the dissociated aryl thio radical, $(Ar\overset{\cdot}{S})$, might be important

in determining the rate of dissociation of the particular initiator.

Of the various disulfides, tetra alkyl thiuram disulfides were

found to be capable of initiating thermal polymerization of styrene and

methyl methacrylate in the temperature range of $50-90^{\circ}$c, but not of

vinyl acetate and acrylonitrile[36,38-40]. Ferrington and Tobolsky[38]

studied the thermal polymerization of methyl methacrylate at 70°c using

tetramethyl thiuram disulfide (TMTD), $(CH_3)_2-N-\overset{S}{\overset{\|}{C}}-S-S-\overset{S}{\overset{\|}{C}}-N-(CH_3)_2$ as

the initiator, and found it somewhat less active than benzoyl peroxide.
TMTD is the only disulfide studied in detail as a polymerization
initiator. A plot of the square of polymerization rate against TMTD
concentration deviated markedly from linearity at rather low concen-
trations of the initiator[38]. Otsu and Nayatani reported an initiator
exponent of about 0.37 in styrene polymerization. It is believed that,
besides bimolecular termination of the growing chains, other modes of
termination are significant, particularly at high initiator concentra-
tion. This presumably involves termination by reaction with TMTD mole-
cules. It has been established that the retardation of polymerization
in this system is due to the initiator molecules rather than to their
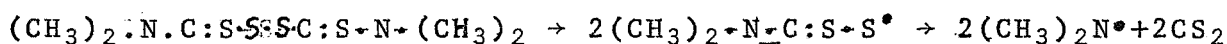decomposition products.

Using low concentrations of TMTD in azobisisobutyro-nitrile-init-
iated polymerization at 70°c and neglecting retardation of polymeri-
zation due to the thiuram disulfide molecules, Ferrington and Tobolsky[38]
reported chain-transfer constants for the above disulfide at 70°c for
methyl methacrylate and styrene as 1.15×10^{-2} and 1.36×10^{-2} respec-
tively.

Initiator transfer is important for many of the sulfur-containing
initiators, and this is significantly of the degradative type. Some of
these compounds, as discussed above, are fairly efficient initiators,
and in all probability the radicals derived from primary dissociation
are different from those produced in chain transfer (radical displace-
ment) reactions. In the case of tetra methyl thiuram disulfide, the

radical displacement may be considered to take place as follows:

$$\_P^{\bullet} + \left[(CH_3)_2NC:S\dot{:}S\right]_2 \rightarrow \_PC:SN(CH_3)_2 + (CH_3)_2NC:S\dot{S}S^{\bullet}$$
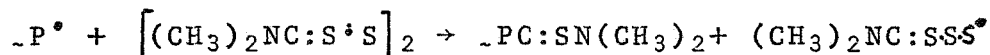
whereas direct dissociation is believed to produce the unstable radical $(CH_3)_2NC:SS^{\bullet}$ which further decomposes to the $(CH_3)_2N^{\bullet}$ radical and carbon disulfide:
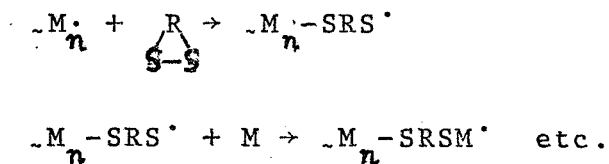
$$(CH_3)_2\dot{:}N.C:S\dot{S}\dot{S}C:S\dot{+}N\dot{+}(CH_3)_2 \rightarrow 2(CH_3)_2\dot{+}N\underline{}C:S\dot{+}S^{\bullet} \rightarrow 2(CH_3)_2N^{\bullet}+2CS_2$$

Tetramethyl thiuram monosulfide is found to be an inijator but not a retarder, while the corresponding tetrasulfide behaves as a retarder but not an initiator. Thus it is believed[36] that retardation is due to polysulfide radicals $RS^{\bullet}_x$ ($x > 1$) which are unreactive towards monomer. The degradative chain transfer reaction of disulfides, e.g., dipjenyl disulfide, may be expressed as:

$$\_P^{\bullet} + (C_6H_5\dot{:}S)_2 \rightarrow \mathscr{P}\cdot C_6H_5 + C_6H_5\dot{:}S\dot{:}S^{\bullet}$$
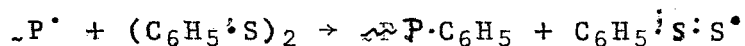
the disulfide radical being unreactive[36]; direct dissociation is understood to involve scission of the S-S bond to give reactive radicals.

It appears in general that thermal or photochemical activation of disulfides results in the cleavage of the S-S bond. This is substantiated by end-group analysis of the polymers (2Rs end-groups per polymer molecule) in certain cases[35] and also by experiments using ring disulfides. In the latter case the observed incorporation of a large amount of sulfur in the polymer is explained[41,42] by considering chain

extension due to copolymerization at each instance of chain transfer involving the ring disulfide:

$$\sim\!\underset{n}{M}\cdot \;+\; \underset{S-S}{\triangle}\!R \;\rightarrow\; \sim\!\underset{n}{M}\cdot\!-SRS\cdot$$

$$\sim\!\underset{n}{M}\!-SRS\cdot \;+\; M \;\rightarrow\; \sim\!\underset{n}{M}\!-SRSM\cdot \quad etc.$$

Dinaburg and Vansheidt[43] studied the chain-transfer capacity of a large number of thiols or mercaptans (RSH) and disulfides (R_2S_2) at $99^{\circ}c$. It was observed that aromatic groups in positions adjacent to an SH group greatly increase the activity of alkyl thiols, but direct-attachment of the SH group to an aromatic ring reduces the activity. Disulfides of the aliphatic series have low activity but aryl and heterocyelic deviatives are quite active.

Among the polysulfides, dimethyl tetrasulfide has been studied[44,45] in some detail with respect to its participation in radical reactions. Dimethyl tetrasulfide decomposes and disproportionates primarily into a mixture of dimethyl tri-, tetra-, penta-,hexa- and probably higher poly-sulfides[44] at $80^{\circ}c$. With the use of very low concentrations of dimethyl tetrasulfide ($< 5\text{-}6 \times 10^{-5}$ m/l) acceleration of the thermal $(80^{\circ}c)$ polymerization of methyl methacrylate and acrylonitrile has been observed. At higher concentrations of the tetrasulfide, pronounced retardation of polymerization occurs. Thus dimethyl tetrasulfide acts simultaneously as a weak initiator and a strong chain-transfer agent of the degradative type. Its apparent chain-transfer contant for acrylonitrile polymeri-zation at $80^{\circ}c$ is reported[44] to be 0.69. The thermal decomposition of

dimethyl tetrasulfide is suggested to take place as follows:

$$CH_3-S_4-CH_3 \rightarrow CH_3\overset{\bullet}{S}_x + CH_3\overset{\bullet}{S}_{(4-x)}$$
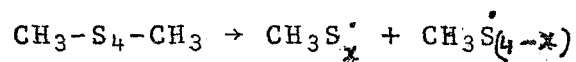
Subsequent disproportionation occurs by the interaction of these radicals and the sulfide. The slow formation of dimethyl disulfide during the latter process may be due to a slower rate of production of the methyl-thiyl radical $CH_3S^\bullet$ in the reaction mixture. It is probably this radical which leads to initiation of polymerization.

Polymers having sulfur-bearing end groups, obtained by using various disulfides or mercaptans as initiators or chain-transfer agents, exhibit good initiator or chain-transfer activity during photo- or thermal polymerization of other monomers in their presence. Block copolymers of methyl methacrylate or acrylonitrile with polystyrene were easily obtained by using sulfur end group-bearing polystyrene (initiated by tetramethyl thiuram disulfide) as the photoinitiator[46]. There are also reports[47,48] in the literature of the easy and efficient sysnthesis of graft-copolymers where the preformed polymer used is a copolymer containing 1-5 mole percent of glycidyl methacrylate; the epoxy side groups in these copolymers are easily transformed into two adjacent pendant SH groups by reacting with a mercapto acid such as mercapto acetic acid or mercapto propionic acid.

The role of mercaptans as chain-transfer agents in free-radical polymerization is well known. Recently Hirahara and coworkers[49] reported a rate-depressing effect of mercaptans on the butyl lithium-initiated aniomic polymerization of methyl methacrylate. The mercaptans used in

small quantities were present in the system as the corresponding lithium mercaptide:
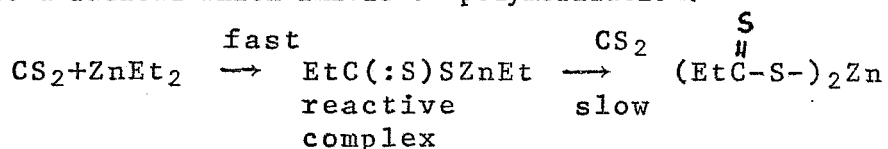
$$BuLi + RSH \rightarrow BuH + RSLi$$
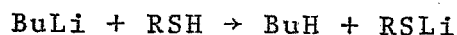
Depression of the polymerization rate in the presence of mercaptides is probably due to the formation of a somewhat stabilized complex between the mercaptide and the active center of the polymerizing monomer. The stereospecificity of the resultant polymer was also affected (increased isotacticity) by the presence of the mercaptides, this effect being in the order of n-propyl < isopropyl < t-butyl < phenyl mercaptide. This observation is in agreement with the idea that stereospecificity of the polymerization is determined by the rigidity of the complex formed at the active center of the polymerizing monomer.

Photosensitive polymers having xanthate end-groups ($-\overset{S}{\underset{}{C}}-O-$) have been easily obtained by using a number of xanthate compounds as photosursitizers[50]. From end-group analysis of such polymers, it is understood that the xanthate compounds of the type RS.C(S)OR' decompose to RS' and C(:S)OR' radicals on photolysis. Polystyrene prepared in the presence of xanthate initiators has been effectively photografted with poly (methyl methacrylate) (grafting efficiency $\approx$ 72-95%) by chain transfer[49]. Photosensitive polymers of similar kind have also been prepared by using acyldithiocarbamates as thermal or photo initiators[51].

Makimoto et.al.[52] reported a cocatalyst effect of carbon disulfide in vinyl polymerization initiated by organometallic compounds, such as
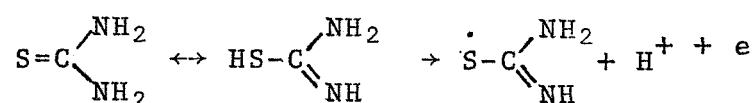
diethyl zinc, diethyl cadmium, and trialkyl aluminum, in diethyl ether

or tetrahydrofuran solution. Instantaneous coloration developed on

mixing carbon disulfide and the organometallic compounds at $0°c$; addition

of methyl methacrylate at room temperature in this colored solution

produced polymer to 10-70% yield in 25-70 hours. Yields thus obtained

were much higher then in systems having no carbon disulfide. The coca-

talyst effect was also observed in the polymerization of methyl acrylate,

styrene, vinyl acetate and acrylonitrile. Formation of a complex inter-

mediate, e.g., Et C (:S) S ZnEt with Zn Et_2 and carbon disulfide was

considered. It was suggested that this intermediate decomposed to pro-

duce a radical which initiated polymerization:

$$CS_2 + ZnEt_2 \xrightarrow{\text{fast}} \underset{\substack{\text{reactive} \\ \text{complex}}}{EtC(:S)SZnEt} \xrightarrow[\text{slow}]{CS_2} (Et\overset{S}{\overset{\|}{C}}-S-)_2 Zn$$

Brown and White[53] described the use of thiourea-monomer canal

complexes as molecular templates for carrying out selective and stereo-

specific polymerization. It was difficult to initiate polymerization by

heat, light and initiators, but irradiation with ionizing radiation

produced high melting crystalline 1,4 trans polymers in good yield from

canal complexes of 2,3 dimethyl butadiene, 2,3 dichlorobutadiene and

1,3 cyclohexadiene. Numerous other monomers forming canal complexes with

thiourea could not be polymerized, however. Thus the scope of polymeri-

zation in thiourea canal-complexes is quite limited due to substrate

specificity. The technic involved specific orientation and possible

activation of the monomers by the complex to obtain highly regular poly-

mers. A fine matching between the size and shape of the monomer and

the size and shape of the canals was required for polymerization to take place.

Thiourea has also been used as an activator in redox initiator systems for aqueous polymerization; e.g., with hydrogen peroxide, persulfate, ferric salts and bromates[54]. Initiation is believed to take place in such systems, at least in part, through the agency of a radical derived from the reducing agent, i.e., thiourea[54,55].

$$S=C\overset{NH_2}{\underset{NH_2}{\diagup}} \leftrightarrow HS-C\overset{NH_2}{\underset{NH}{\diagup}} \rightarrow \overset{\cdot}{S}-C\overset{NH_2}{\underset{NH}{\diagup}} + H^+ + e$$

In fact poly(methyl methacrylate) samples prepared with redox initiator systems, having thiourea as the reductant, have been found to bear amine end-groups to significant extents. The structure of the radical derived from thiourea is believed to be $\overset{\cdot}{S}$-C(:NH)-NH$_2$ instead of $\overset{\cdot}{HN}$-C(:S)-NH$_2$; this is confirmed by Mandal et.al.[55] by the fact that on treating the amino-end group-bearing polymers in acetone solution with alcoholic alkali under mild conditions and subsequent purification, the response to amino-end group becomes negative and the molecular weight of the polymer increases by a large extent. The increase in molecular weight may be partly due to the formation of disulfides from the macro-molecular mercaptans resulting from the alkali treatment of the original polymer (polymeric S-alkyl thiourea):

$$\sim\!\!\sim\!S-C\overset{NH_2}{\underset{NH}{\diagup}} \xrightarrow{\text{alkali}} \sim\!\!\sim\!SH \xrightarrow{[O]} \sim\!\!\sim\!S-S\!\sim\!\!\sim$$
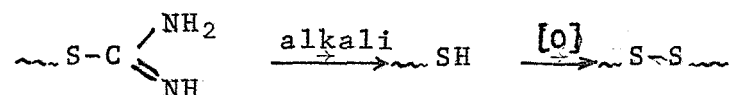
Sulfuric acid

The use of sulfuric acid as a catiomic catalyst for polymerization

is well known. Pepper and coworkers[56-59] studied the cationic polymeri-
zation of styrene in 1,2-dichloroethrylene solution at 0-25°c, using
sulfuric acid as the cationic initiator. The final yield of polymer
was low in this temperature range. The polymerization features were
found to be different from those of a normal steady-state chain reac-
tion. The rate of polymerization was very fast and was dependent on
acid concentration but independent of monomer concentration, and the
average molecular weights of the polymers were fairly low[57] (20,000).
The results were explained on the basis of a non-steady-state chain-
reaction theory developed for the purpose[56]. The effect of the presence
of certain additives on rate was studied and evidence was found that
polar substances interacted to varying degrees (depending on their
polarity) with the catalyst as well as with the growing carbonium
ion[59]. Molecular weight was determined, by and large, by chain trans-
fer, rather than by chain termination.

Tsuda[60] observed in the sulfuric acid-initiated polymerization of
styrene in methylene dichloride that the molecular weight could be
greatly increased by lowering the temperature. Water was found to be
a strong inhibitor in sulfuric acid-catalysed polymerization. This
was explained by considering transfer of protons to water molecules
from the active proton dornor in the system:

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$
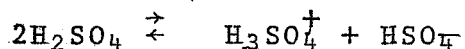
$$H_3SO_4^+ + CH_2=CH\phi \rightarrow CH_3-\overset{+}{C}H\phi + H_2SO_4 ,$$ and in the
presence of water;

$$H_3SO_4^+ + H_2O \rightarrow H_2SO_4 + H_3\overset{+}{O}$$
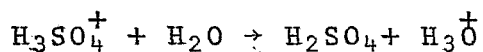
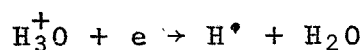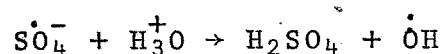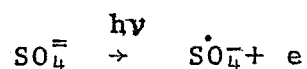$H_3\overset{+}{O}$ is a weak proton donor; hence the transfer of a proton to the monomer to form a carbonium ion is suppressed. Friedel-Crafts catalysts are themselves strong acids but their hydrates are active proton donors. Therefore, water behaves as a cocatalyst in Friedel-Crafts catalyst systems as opposed to its inhibitory effect in sulfuric acid-catalyred systems:[60]

$$BF_3 + H_2O \underset{\rightarrow}{\rightarrow} BF_3 \cdot H_2O$$

$$BF_3 \cdot H_2O + M \rightarrow MH^+ + BF_3 \cdot OH^-$$
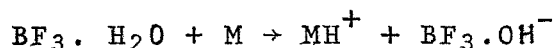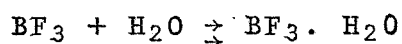
Sulfuric acid at low concentration (0.1-0.001 m/l) in deaerated aqueous solution was found[61,62] to polymerize methyl methacrylate slowly in the presence of sunlight or ultraviolet light after a long inhibition period. Trace amounts of sulfate end-groups were detected in the polymer. Polymerization was believed to take place primarily by $\overset{\cdot}{O}H$ radicals and hydrogen atoms formed in the medium according to the following scheme:

$$SO_4^= \overset{h\nu}{\rightarrow} \overset{\cdot}{SO_4^-} + e$$

$$\overset{\cdot}{SO_4^-} + H_3^+O \rightarrow H_2SO_4 + \overset{\cdot}{O}H$$

$$H_3^+O + e \rightarrow H^{\cdot} + H_2O$$

It has been reported by Barret et.al.[63] that the net result in the photolysis of sulfate ions in aqueous medium is the photo-dissociation of water molecules.
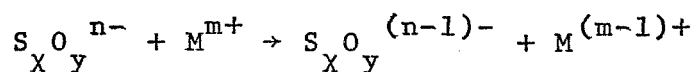
Salts of reducing sulfoxy compounds

Sulfurous acid (H_2SO_3) and sodium sulfite (Na_2SO_3) were observed to be very sluggish and inefficient initiators of aqueous polymerization of methyl methacrylate, but sodium bisulfite ($NaHSO_3$) was found to be an efficient aqueous initiator with monomer selectivity[64]. Methacrylate monomers were easily polymerized at 0–$30^{\circ}c$; polymerization of styrene was very slow and sluggish. No polymerization was observed with vinyl acetate, acrylonitrile or the acrylates as the monomer. Initiation of polymerization is believed[64] to be due to sulfonate ion radicals derived from a redox reaction between the bisulfite ion and monomer molecules. Sodium metabisulfite ($Na_2S_2O_5$) and sodium dithionite ($Na_2S_2O_4$) were also found to initiate the aqueous polymerization of methyl methacrylate, and polymers were found to bear nonhydrolyzable sulfonate-type anionic end-groups.[64,65]

All the above reducing sulfoxy compounds as well as alkali thiosulfate form efficient redox initiator systems with persulfates. Polymerization is initiated by radicals derived from both the oxidant and reductant, as evidenced by end-group analysis[66]:

$$S_2O_8^{=} + S_xO_y^{n-} \rightarrow SO_4^{=} + SO_4^{-} + \dot{S}_xO_y^{(n-1)-}$$
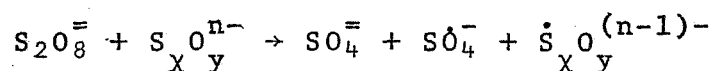
In redox systems involving the reducing sufloxy compounds and oxidizing metal ions, the primary initiating radicals are derived from the sulfoxy compounds as follows:

$$S_X O_y^{n-} + M^{m+} \rightarrow S_X O_y^{(n-1)-} + M^{(m-1)+}$$

and anionic sulfonate-type end-groups have been detected in the polymers obtained[67]. Other redox systems in common use involving the reducing sulfoxy compounds are those having hydrogen peroxide, Oxygen or halate salts as the oxidant. Using a chlorate-sulfite initiator system for the polymerization of acrylamide in acidic aqueous media, Suen et.al.[68] observed that HSO_3^- ion was an active chain-transfer agent, having a transfer constant of 0.17 at 50°c.

Sulfuryl chloride

Sulfuryl chloride (SO_2Cl_2) is known[69] to take part in radical reactions, e.g., the peroxide-induced chlorination of olefins. Sulfochlorination of hydrocarbous has been effected using SO_2Cl_2 and light in the presence of pyridine as a catalyst[70]. Low concentration of sulfuryl chloride were found to initiate the bulk polymerization of methyl methacrylate thermally at 60-80°C, or more efficiently on irradiation with visible or ultraviolet light. The polymers so obtained incorporated chlorine and sulfony end-groups.

Dimethyl sulfoxide

Another interesting sulfoxy compound which is known to

participate in polymerization is dimethyl sulfoxide (DMSO).

The use of alkali metal – DMSO compounds as initiators of poly-
merization has recently been reported[72-75]. The polymerization

behavior of several monomers was examined with sodium-or potassium-

DMSO, and the results were consistant with anionic initiation.

DMSO, having a high solubility parameter and high dielectric

constant, dissolves many monomers and polymers, all of which are

not readily soluble in solvents conventionally used in anionic

polymerization. The order of polymerizability was found to be

acrylonitrile > methyl methacrylate >> styrene, and copolymeri-

zation experiments with the binary system of acrylonitrile and

styrene in equimolar amounts produced almost exclusively the

homopolymer of acrylonitrile[76]. The structure of the anion de-

rived from DMSO (e.g. by reaction with butyl lithium) is as

follows:

$$Bu\overset{-}{L}i^{+} + CH_3-\overset{\overset{O}{\parallel}}{S}-CH_3 \rightarrow CH_3-\overset{\overset{O}{\parallel}}{S}-CH_2Li^{+} + BuH.$$
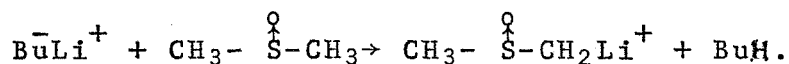
The dimsyl anion, as this anion is called, polymerized acryloni-
trile with almost theoretical yield[73] in homogeneous (DMSO)

solution at $20-50°c$ and molecular weights of the order of

76×10^3 to 185×10^3 were obtained. Termination of growing

chains by transfer with DMSO is an important factor giving rise

to relatively low molecular weight polymers. Styrene poly-

merization generally yielded very low molecular weight oily

polymers. Polymerization to high molecular weights was strongly
inhibited in DMSO due to termination by chain transfer to the
solvent:

$$P_n^{\ominus} + CH_3-\overset{O}{\underset{}{S}}-CH_3 \rightarrow PH + \overset{\ominus}{C}H_2- \overset{O}{\underset{}{S}}-CH_3$$
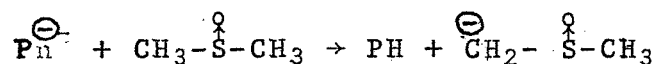
where $P^{\ominus}$ represents a growing (carbonion) chain. The major prod-
uct in styrene polymerization contained one sulfinyl group and
three styrene units, as reported by Gosnell et.al.[75]. They pro-
posed the following mechanisms to explain this: In the growing
chains containing one or two styrene units, the ion-dipole inter-
actions between the sulfoxide group at one end and the ion pair
of the growing end stabilize the intermediates and thereby
decrease the probability of proton abstraction from the solvent
at these two stages of monomer addition. After the addition of
the third monomer unit, this stabilizing interaction is no longer
possible and thus solvent transfer predominates over chain pro-
pagation.

Hydrogen sulfide

The use of hydrogen sulfide in vinyl polymerization is quite
limited. The addition reactions of hydrogen sulfide to define
double bonds under pressure and at high temperatures and that
recurring at low temperature under ultraviolet light are known[77-79].

But formation of high polymers by hydrogen sulfide, behaving as an initiator, has not been reported. The chain-transfer ability of hydrogen sulfide was, however, examined by Britenbach and Olaj[80] in the polymerization of styrene and acrylonitrile. Polymers with significant sulfur content were isolated by thermal catalyzed polymerization of these monomers in presence of a fairly high concentration of hydrogen sulfide. Ulbricht and Sourisseau[81] observed that polyacrytonitrile prepared in the presence of hydrogen sulfide (using axobisisobutyronitrile initiator at 50°c) contained 0.5-2.5% S as end-groups; only 2-6% of this sulfur was in the form of mercapto end-groups, and the rest became incorporated in the polymer chains in a form having no transfer activity. The present author[82] recently examined the ability of hydrogen sulfide to initiate vinyl polymerization and observed that methyl methacrylate formed polymers at a very slow rate at or near room temperature in the presence of very low concentration (10^{-5}-10^{-2}m/l) of hydrogen sulfide used as the initiator[82]. The polymerization was retarded when the concentration of hydrogen sulfide was higher than about 1 x 10^{-3}m/l. Vinyl acetate, acrylonitrile and methyl acrylate did not give any polymer. The chain-transfer constants of hydrogen sulfide at 60°c for the polymerization of methyl methacrylate and styrene were found to be 0.081 and 1.99 respectively[82]. The polymerization by hydrogen sulfide probably involves a complex radical mechanism, i.e., formation of a labile complex between the monomer

and hydrogen sulfide which then slowly dissociates into radicals to
initiate polymerization. The radicals may otherwise give addition
products by recombination under suitable conditions or may lead to
side reactions which suppress polymerization.

Sulfur dioxide

The effect of sulfur doxide on vinyl polymerization has been
studied for some time. The bulk of the published data until recently
was concerned with the use of liquid sulfur dioxide as a medium of
polymerization or as a comonomer in the presence of a vinyl or related
monomer, with a radical or ionic catalyst or some radiation to induce
polymerization[83-91]. Some instances of spontaneous polymerization in
the presence of liquid sulfur dioxide without the advent of any cata-
lyst or radiation are also reported[92,93]. The products of polymeri-
zation obtained in liquid sulfur dioxide are either of the unsaturated
monomer and sulfur dioxide, commonly called a polysulfone.

Sulfur dioxide is known to form complexes with olefinic compounds
and a host of other compounds such as amines, ethers, phenols and aroma-
tic hydrocarbons[94-97]. Liquid sulfur dioxide is also known[98] to
dissociate into ionic species as follows:

$$2SO_2 \leftrightarrow SO^{2+} + SO_3^{2-}$$
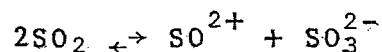
Thus during polymerization in liquid sulfur dioxide, the probable par-
ticipation or influence of any complex or ionic species as mentioned

above should be taken into consideration. Sulfur dioxide behaves as a good electron acceptor and is more reactive in this respect than maleic
~~inactive~~ anhydride at low temperatures, but their reactivities are more or less comparable[99] at about 30°c.

In a liquid sulfur dioxide system, cationic catalysts, such as BF_3, H_2SO_4 etc., lead to the formation of a homopolymer of the unsaturated monomer, while the formation of a polysulfone is brought about in general with the use of free-radical initiators, such as benzoyl peroxide, azobisisobutyronitrile, etc.[83-93]. There have been some reports where simultaneous formation of a homopolymer and a polysulfone are observed[84,88,100], even in presence of a free-radical initiator[88].

In uncatalyzed polymerization of styrene in liquid sulfur dioxide. Barb[84] observed that the percentage of sulfur dioxide in the polymer product decreased as the sulfur dioxide to styrene ratio in the feed solution was increased. Thus in addition to the normal free-radical polymerization leading to the formation of a polysulfone, a cationic polymerization (initiated either by the cationic species of sulfur dioxide or by some reaction of the sulfur dioxide monomer complex), also took place and this process did not incorporate either sulfur dioxide or the complex present in the system into the polymer. More recently Tokura et.al.[88] observed simultaneous radical polysulfone formation and cationic homopolymerization of p-isopropylstyrene in liquid

sulfur dioxide in the presence of arobilisobutyronitrile initiator.

In the presence of dimethyl formamide the cationic homopolymerization was completely inhibited and only a polysulfone was obtained. Schulz and Banihaschemi[101] observed fast polymerization of styrene to sulfur-free polystyrene in liquid sulfur dioxide in the presence of hydro-peroxides and peracids as catalysts, and the polymerization remained uninhibited by hydroquinone or m-dinitro benzene. Polymerization was considered to take place by a cationic mechanism, and the use of solvents such as benzene, toluene and dichloromethane had little effect. The use of nitrile compounds and dimethyl formamide, however, led to the formation of polystyrene sulfone at a much reduced rate. Thus liquid sulfur dioxide appears to be a unique solvent which permits polymeri-zation of olefinic and vinyl compounds by either radical or cationic mechanisms depending on the conditions of polymerization, and sometimes permitting simultaneous radical and cationic polymerization. At the same time the solvent itself participates in the polymerization process either as a comonomer giving rise to polysulfones of rather regular sequence distribution under favorable conditions, and/or as a polar solvent influencing the overall rate of polymerization without being incorporated in the polymer to a measurable extent.

An interesting feature of the radical polymerization of olefines in liquid sulfur dioxide is the ready formation of predominantly 1:1 - alternating copolymers from a range of feed compositions. In the case of cyclohexene[102] the structure of the polysulfone is:
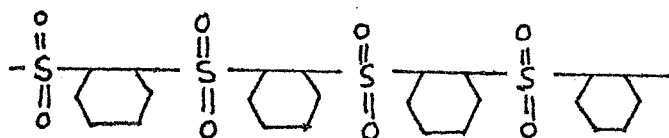
and for unsymmetrical olefins, e.g., propylene and pentene, writing

X = Y for the olefin, the polysulfone has an alternating struc-

ture:[103,104]

$$-X-Y-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-Y-X-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-X-Y-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-Y-X-$$
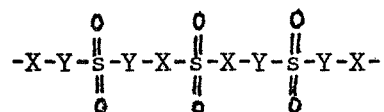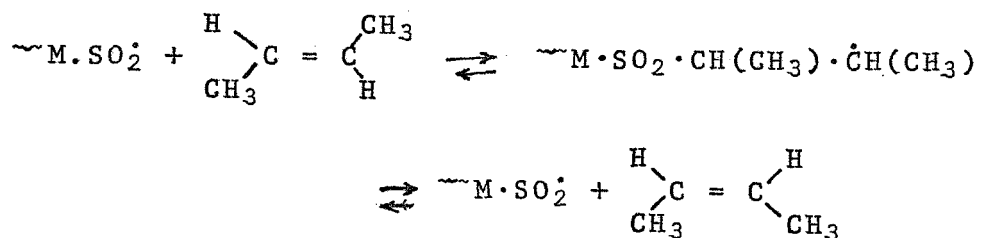
The copolymerization of an olefinic hydrocarbon and sulfur

dioxide is considered to be a simple polymerization of a 1:1 complex

of the two monomers. For styrene and styrene derivatives, 2:1 poly-

sulfones, i.e., 2 monomer units for one SO_2 unit, were normally ob-

tained by radical polymerization[84,88]. Vinyl chloride and vinyl bro-

mide were also reported to give 2:1 polysulfones[105,106].

An important observation in polymerization, first made in connec-

tion with polysulfone formation in liquid sulfur dioxide, is the ceil-

ing-temperature (Tc) phenomenon. Snow and Frey[107] observed that sulfur

dioxide-isobutene mixtures containing a suitable initiator polymerize

at temperatures below 4-6°c, but the reaction stops on warming above

this temperature. The ceiling temperature (Tc) is defined as that

temperature above which monomer cannot be converted into long-chain

polymer. Thermodynamically, it is the temperature at which the free

energy of polymerization is zero. In the polymerization of styrene in

liquid sulfur dioxide, the reaction incorporating sulfur dioxide in

the polymer competes with the normal chain-propagation process to yield

polystyrene, and a phenomenon analogous to ceiling temperature is ob-

served in that the amount of SO_2 incorporated in the copolymer decrease

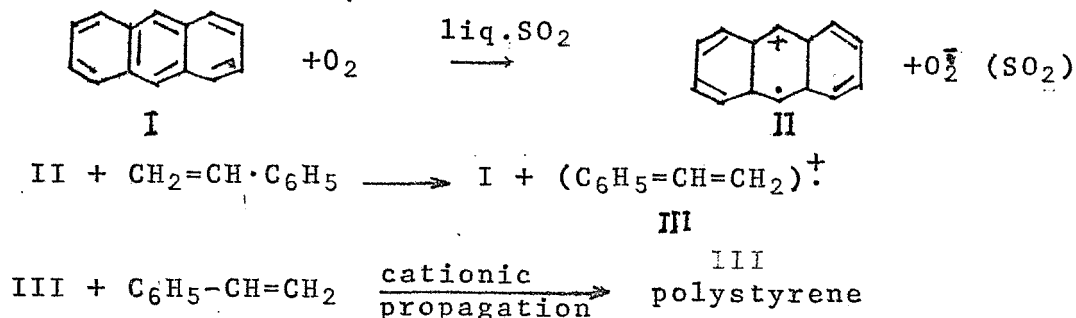markedly with temperature. The dependence of polysulfone composition

on temperature and the concentrations of monomers (styrene and sulfur dioxide) was explained by Barb[84] in terms of reversible propagation and inclusion of SO_2 in the copolymer exclusively by reaction of a growing chain with a 1:1 complex of styrene and SO_2. Walling[108], however, explained it by an alternative scheme not involving the participation of a styrene-SO_2 complex. Based on rate measurement and the temperature dependence of copolymer composition in a styrene-sulfur dioxide system at elevated temperatures, Barb[84] estimated the activation energy of the depropagation reaction involving the breakage of a carbon-sulfur bond as 12-15 Kcal, which is much lower then that for the depropagation of a vinyl polymer.

A penultimate unit effect has been recognized in the copolymerization of styrene and sulfur dioxide. SO_2 fails to add to a radical with a terminal SO_2 unit and moreover it also fails to react to a polymer radical in which SO_2 is the penultimate unit[84,108].

The copolymerization of sulfur dioxide with cis- or trans- 2-butene is accompanied by isomerization of the respective olefin[109]. The rate of isomerization increases as the temperature approaches the ceiling temperature despite decrease in the rate of polymerization. The effect is interpreted in terms of the propagation depropagation equilibria:

$$\sim M \cdot SO_2^{\cdot} + \underset{CH_3}{\overset{H}{\diagdown}} C = C \underset{H}{\overset{CH_3}{\diagup}} \rightleftharpoons \sim M \cdot SO_2 \cdot CH(CH_3) \cdot \dot{C}H(CH_3)$$

$$\rightleftharpoons \sim M \cdot SO_2^{\cdot} + \underset{CH_3}{\overset{H}{\diagdown}} C = C \underset{CH_3}{\overset{H}{\diagup}}$$

The instantaneous polymerization of styrene in liquid SO_2 to sulfur-free polystyrene at a fast rate in the presence of anthracene and oxygen was reported by Tokura and coworkers[110]. Rapid initiation could not be effected in the absence of either anthracene or oxygen and the polymerization was inhibited in the presence of dimethyl sulfoxide, an inhibitor for cationic polymerization. Initiation of polymerization was considered to take place through the agency of cation radicals $(C_6H_5CH = CH_2)^{\overset{+}{\cdot}}$ formed in the system according to the following scheme:

$$II + CH_2=CH \cdot C_6H_5 \longrightarrow I + (C_6H_5=CH=CH_2)^{\overset{+}{\cdot}}$$
$$III$$

$$III + C_6H_5-CH=CH_2 \xrightarrow[\text{propagation}]{\text{cationic}} \overset{III}{\text{polystyrene}}$$

Overberger and Moore[111] reported the formation of a yellow color when benzyl vinyl sulfide was added to liquid sulfur dioxide in the presence of air; a 1:1 polysulfone was isolated from this system. But in the absence of air no coloration was observed and only a minute trace of a solid polymeric product was isolated; this was not a 1:1 polysulfone. Polymerization by a radical mechanism via the formation of a charge-transfer complex (yellow color) between the monomer and sulfur dioxide is believed to take place in the presence of air.

Polymerization of acrylonitrile in liquid sulfur dioxide in the presence of a radical initiator at 50°c produced[112] only the homopolymer

of acrylonitrile instead of the expected copolymer (polysulfone).

Tokura et.al.[112] explained this by considering a positive charge on

the monomer due to the presence of the electron-attracting nitrile

group and thus precluding formation of a charge-transfer complex be-

tween the monomer and sulfur dioxide. Similar radical homopolymeriza-

tion was also observed[113] for methyl methacrylate in liquid sulfur

dioxide.

It is interesting to note[114] here that radical polymerization

of m-bromostyrene in liquid SO_2 gives polysulfones with sulfur con-

tents well below that observed in styrene-SO_2 system and no SO_2 is

incorporated in the polymer when p-nitro styrene is radically poly-

merized in liquid SO_2 . It is thus indicated that styrene derivatives

having electron withdrawing groups and having e values larger than the

e value of styrene, have less or no tendency to copolymerize with SO_2.

Matsuda and coworkers[115,116] reported retardation of the radical

polymerization of acrylonitrile in liquid sulfur dioxide due to the

presence of aniline and other aromatic amines, due to chain transfer of

the degradative type. This chain transfer is more pronounced in

liquid sulfur dioxide than in benzene; this is attributed to the differ-

ences in polarity of the terminal radicals of the growing chains in

the two solvents. The chain-transfer constants for three amines in the

above two solvent systems[115,116] are given in Table I.

It is interesting to note a polymolecular dependence of the over-

all rate of styrene polymerization on sulfur dioxide concentration as

Table I

Comparison of chain-transfer constants C_{tr} of three
aromatic amines in the polymerization of acryloni-
trile in liquid sulfur dioxide and benzene.

C_{tr} in benzene	Aromatic amine	C_{tr} in liquid SO_2
4.40×10^{-3}	Aniline $(50^{\circ}c)$	0.96
9.64×10^{-2}	Dimethyl aniline $(60^{\circ}c)$	2.18
5.47×10^{-2}	Diethyl aniline $(60^{\circ}c)$	14.32

reported by Tokura et.al.[83] for cationic polymerization in liquid

sulfur dioxide. In the presence of certain solvents, the rate R_p was

expressed as: $R_p = $ constant x $(solvent)^n$. Solvents for which n is nega-

tive (benzene: -1.5, toluene: -0.8, p-xylene: -0.8, p-cymene: -0.3)

behave as acceptors of cations; they presumably interact with the

catonic end of the growing chains and form a relatively stable complex

with liquid sulfur dioxide and thus retard the polymerization rate.

Other solvents having positive values of n (cyclohexane: 0.7 and chloro-

benzene: 0.4) are found to accelerate the rate, solvents of this class

are considered neutral or bear positive charge and do not interact with

the growing cationic centers or SO_2 but act rather to repel them.

The effect of liquid-sulfur dioxide concentration on the relative

reactivity of monomers in the cationic copolymerization of styrene (M_1)

and methyl acrylate (M_2) at $0°C$ using BF_3, Et_2O complex as the cationic

initiator was studied by Matsuda et.al.[91]. The monomer reactivity ratio

r_1 changed from 0.30 at $(SO_2) = 6.58$ m/l to $r_1 = 1.50$ at $(SO_2) = 13.16$

m/l, but r_2 remained unchanged. Using the same catalyst system in the

cationic copolymerization of styrene (M_1) and α-methyl styrene (M_2),

Iino and Tokura[90] observed that r_1 and r_2 at $-40°c$ in liquid sulfur

dioxide were 0.0 - 0.1 and > 20, respectively, while the corresponding

values were 0.2 - 0.3 and 12 ± 2 in methylene chloride at $-20°c$. The

copolymer composition and monomer sequence distribution were determined

by NMR spectroscopy. The fraction of isolated single styrene units

spaced between two α-methyl styrene units (alternating structure) was

calculated by a comparison of the phenyl doublet and phenyl singlet

absorptions. In methylene chloride medium, the alternating structure

accounted for 38.3% of the styrene units in the copolymer from a

nearly equimolar amount of the two monomers in the feed. On the other

hand, the copolymer produced in liquid sulfur dioxide seemed to be a

non-alternating copolymer having practically no lone styrene units

spaced between two α-methyl styrene units. These effects were explain-

ed in terms of the greater degree of solvation of styrene molecules in

liquid sulfur dioxide compared to α-methyl styrene molecules, and

the higher reactivity of α-methyl styrene toward carbonium ions in

liquid sulfur dioxide.[90]

Tokura and Kawahara[117] reported the interesting observation that

alkyl and aralkyl halides, such as ethyl, n-propyl, isopropyl, n-butyl,

t-butyl, -phenethyl and benezyl chloride, are all effective catalysts

for the cationic polymerization of styrene in liquid sulfur dioxide.

No Lewis-acid catalyst was used and only homo-polystyrene was obtained.

The production of free carbonium ions from the alkyl chlorides is not

conceivable in ordinary solvents, but a strong solvation of chloride anion

by liquid sulfur dioxide may be operative, and carbonium ions derived

from the alkyl groups probably initiate polymerization in liquid sulfur

dioxide[117]; the exact mechanism is not clear however.

Tokura et.al.[89] observed increased inhibition and subsequent re-

tardation of radical polymerization in a liquid sulfur dioxide - dimethyl

sulfoxide (DMSO) solvent system when potassium iodide was added to the

system. This effect was caused by the formation of iodine in the KI-

DMSO - SO_2 system as visually demonstrated by the development of iodine

color in the solution. No coloration was noticed, however, in either

the KI - DMSO or KI -liq -SO_2 binary system. The possible mechanism of

the formation of iodine is:

$$2KI + (CH_3)_2 SO + SO_2 \longrightarrow (CH_3)_2 S + K_2SO_3 + I_2$$

Polymerization of olefinic, allylic and vinyl compounds in liquid

sulfur dioxide induced by γ-irradiation in absence of any radical or

ionic catalysts was normally found to occur by a radical mechanism

giving rise to the respective polysulfones[86,118-120].

Stille and Thomson[121] studied radical copolymerization of a non-

conjugated diene (1.5 hexadeine) and sulfur dioxide and found that

two sulfur dioxide units were present for each diolefin unit in the

resulting copolymer. Each sulfur dioxide molecule presumably complexed

with one double bond of the diolefin prior to polymerization. The pro-

posed propagation mechanism involved a cyclocopolymerization through

the intermediary of these complexes, corresponding to alternating intra-

molecular - intermolecular bi-radical propagation. The structure and

formation of the linear copolymer may be represented as:

complex formation

propagation / complex

Linear polymer

biradical
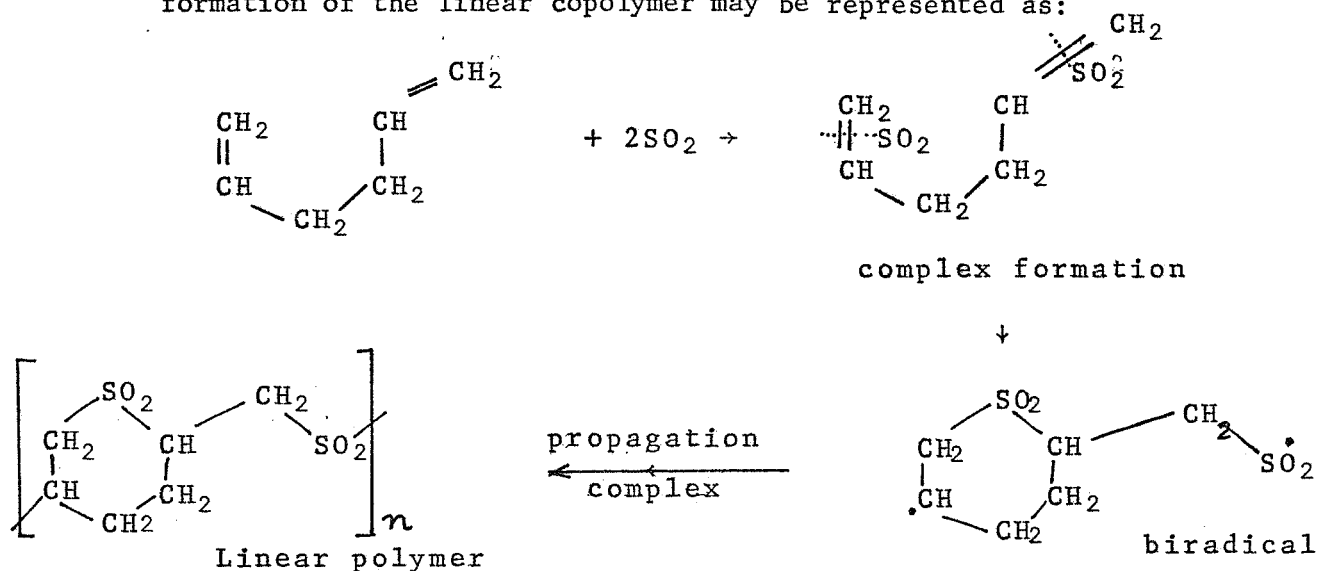
Zutty and coworkers[92,122] reported a spontaneous copolymerization
of bicyclo-2,2,1,hept-2-ene and sulfur dioxide at low temperatures.
Polymers were obtained in high conversion ($\simeq 93\%$) in a matter of minutes;
the molecular weight of the copolymer increased with conversion and
time; the reaction could not be inhibited indefinitely without exhaust-
ing one of the monomers; and a high concentration of radicals was
detected in the system by electron paramagnetic resonance studies. The
polymerization may be considered to take place through the intermediary
of charge-transfer complexes formed between the reactants followed by
rearrangement of the complex to a biradical and fast propagation to
copolymer by biradical coupling:
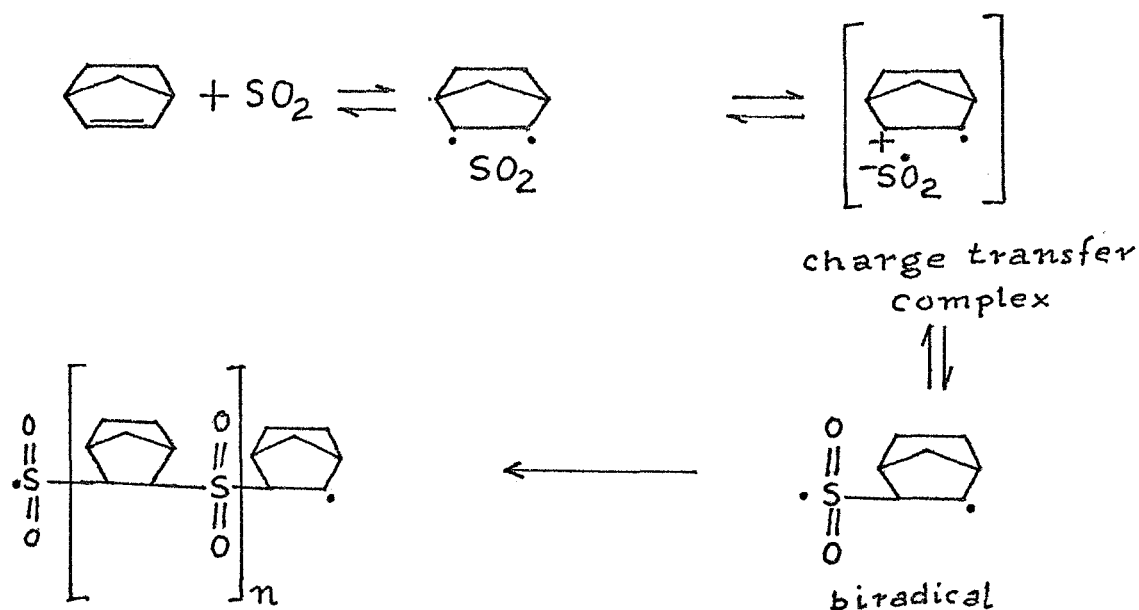
Living polymers would be the expected result according to this mechanism,
and this was substantiated experimentally by the formation of a block

copolymer on addition of a third monomer such as ethyl acrylate in the living polysulfone system.

With N-vinyl carbazole as the monomer, Solomon et.al.[93] observed that the polymer obtained in liquid sulfur dioxide at $-15^{\circ}c$ in the absence of a catalyst was a homopolymer of the carbazole, irrespective of conversion. Although the exact mechanism of polymerization is not clear, it is believed that the prolymerization reaction took place by an ionic mechanism. Frazer[123] reported a case of radical terpolymerization of an α-olefin, sulfur dioxide and carbon monoxide under high pressures (1000-3000 atmospheres) and at temperatures above the ceiling temperature of the particular α-olefin-sulfur dioxide system.

Matsuda and coworkers[124,125] studied the polymerization of methyl methcrylate, styrene and methyl vinyl pyridine initiated by charge-transfer complexes of sulfur dioxide and pyridine or pyridine derivatives in liquid sulfur dioxide in the presence of an organic halide such as carbon tetrachloride. No initiation was observed in the absence of the charge-transfer complex or of carbon tetrachloride. Inhibition of polymerization was observed in the presence of hydroquinone for styrene or methyl vinyl pyridine but not for methyl methacrylate. For the polymerization of methyl methacrylate, the overall rate was found to be proportional to the square root of the concentration of the sulfur-dioxide - pyridine complex and to the 1.5 power of the monomer concentration. Based on the polymerization kinetics it was suggested that a primary radical was produced from the reduction of carbon tetrachloride

by an associated sulfur dioxide – pyridine – monomer complex[123].

Later Bamford et.al.[126], based on their observation on halide dependence of polymer yield in the above system, found it necessary to postulate that free sulfur dioxide (not complexed with pyridine) was an important component of the initiating system at all halide concentrations. Observation of a rate-enhancing effect of dimethyl formamide indicated that polar species were formed as intermediates during polymerization. The initiation mechanism suggested by Matsuda and Hirayama[123] more or less conforms to the experimental observations.

Ghosh and O'Driscoll[127,128] reported the use of sulfur dioxide in catalytic concentrations (10^{-4}-10^{-1} m/l) as an initiator of vinyl polymerization. Polymerization of methyl methacrylate, ethyl methacrylate, n-butyl methacrylate and styrene was effected slowly at or near room temperature while other monomers, such as vinyl acetate, acrylonitrile, and alkyl esters of acrylic acid, could not be polymerized under similar conditions. The polymerization rate for methyl methacrylate was found to pass through a maximum when plotted against sulfur dioxide concentration. Employing a tracer technique, about 0-2 sulfur atoms per chain was detected in the polymers when the concentration of the initiator sulfur dioxide was less then 10^{-2} m/l, the molecular weights
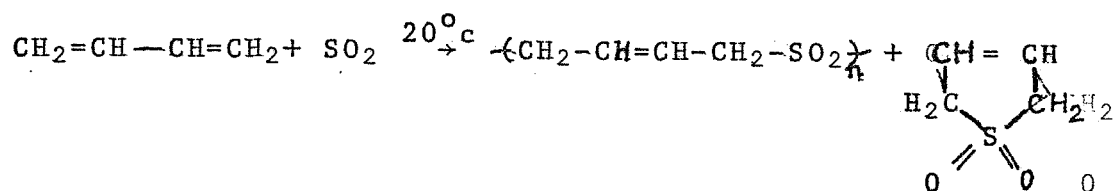
of the polymers having been in the range of $(3-12) \times 10^6$.
At much higher sulfur dioxide concentration, higher in-
corporation of sulfur dioxide in the polymer, probably by
way of copolymerization in part, was obtained[128].

A hydroperoxide, such as t-butyl hydroperoxide greatly
accelerates the sulfur dioxide-activated polymerization of
methyl methcrylate and other vinyl monomers. Diphenyl picryl
hydrazyl and hydroquinone do not inhibit the hydroperoxide-
sulfur dioxide-initiated polymerization of methyl methacry-
late. End-group analysis indicates that the initiation of
polymerization is brought about by sulfonate and hydroxyl
radicals. Inert solvents such as benzene and toluene enhance
the rate of polymerization of methyl methacrylate but not of
other monomers, as observed by Ghosh and Billmeyer[129]. An
initiation mechanism involving the initiators, monomer and
solvent appears predominent in the case of methyl methacry-
late while with other monomers, an initiation mechanism
involving only the initiators and monomer is predominent.

A preliminary study of the graft copolymerization of
methyl methacrylate on 1,4 cispolyisoprene has been made by
the author in this laboratory and the results are given in
Table II. It is seen that the formation of graft copolymer
is largely dependent on both sulfur dioxide and polyisoprene

concentration. Comparing the grafting efficiencies E_p and E_m (i.e., grafting efficiencies based on total polyisoprene present and total poly (methyl methacrylate) formed respectively) it is apparent that higher degrees of grafting are favored at lower concentrations of polyisoprene and higher concentrations of sulfur dioxide in the system. The grafting efficiencies were determined by following the analytical procedure described by Ghosh and SenGupta[130]. The mechanism of graft formation apparently involves charge-transfer-complex formation between sulfur dioxide and the polyisoprene unsaturation (as evidenced by the development of a light-yellow color in the system when frozen in liquid nitrogen, While no color formation is observed when polyisoprene is absent from the system). Radical sites on polyisoprene chains derived from the rearrangement of the charge-transfer complexes serve as centers for the initiation of graft copolymerization.

An interesting case of "decomposition polymerization" of a cyclic sulfone has been reported recently by Minoura and Nakajima[131] and Goethals[132]. It is known that the reaction between sulfur dioxide and butadiene produces a cyclic crystalline adduct in addition to a linear amorphous polysulfone:

$$CH_2=CH-CH=CH_2 + SO_2 \xrightarrow{20^{\circ}c} (CH_2-CH=CH-CH_2-SO_2)_n + \underset{\underset{O}{\overset{\displaystyle S}{\underset{O}{\parallel}}}{\overset{\displaystyle CH=CH}{\underset{\displaystyle H_2C\quad CH_2}{}}}$$

                                        butadionene sulfone
                    11%   89%

Table II

Sulfur dionide-initiated graft copolymerization of

methyl methacrylate and 1.4 cispolyisoprene

Temperature: $30^{\circ}c$, benzene: 10 ml.

methyl methacrylate (MMA):3 ml.

Expt No.	C Cis polyiso-prene gm	SO_2 m/l	Time hr.	Total PMMA formed gm	Free polyiso-prene in pro-duct gm	%Grafting ic-inefficiency	
						E_p	E_m
1	0.3160	0.023	160	nil	0.3154	---	---
2	0.3032	0.230	94	0.0387	0.2870	9.1	76.7
3	0.3122	0.023	94	nil	0.3120	---	---
4.	0.1085	0.230	160	0.2735	0.0804	25.9	92.6
5	0.1085	0.023	160	0.2169	0.0866	20.2	97.6
6	None	0.023	160	0.0214	---	---	---

The cyclic product, butadiene sulfone, is found to polymerize only radically above $80^{\circ}c$, the radical initiators used being azobisisobutyronitrile and trialkyl boron. Polymerization at $80-140^{\circ}c$ yields rubberlike polymers, insoluble in organic solvents. The polymer composition (butadiene to sulfur dioxide ratio) is independent of monomer and initiator concentrations and reaction time, but dependent on temperature, giving lower percentages of sulfur in the polymer at higher temperatures. It is known that butadiene and sulfur dioxide are formed by the thermal decomposition of butadiene sulfone[133]. A suitable mechanism for the polymerization of butadiene sulfone at high temperature in the presence of radical initiators, therefore, appears to be the formation of butadiene and sulfur dioxide by its thermal decomposition and subsequent radical copolymerization of the decomposition products. The mechanism is thus a "decomposition polymerization" as opposed to a "ring-opening polymerization".

Recently Schaefer et.al.[134] have reported copolymerization of propylene oxide and sulfur dioxide using a variety of catalysts such as $Sncl_4$, Et_2Zn and $Sbcl_5$ at about $55-60^{\circ}c$ to form a new type of copolymer, the poly (sulfite ether),

$$\left[\begin{matrix} O \\ \| \\ S-O-CH(CH_3)CH_2-O \end{matrix}\right]_n$$

. The monomer distributions in low-conversion copolymers have been determined from NMR analysis and gas-liquid partition chromatography of the glycol ethers resulting

from the hydrolysis of the copolymers. Hydrolysis experiments indicate that the primary structure of the links between the two monomer segments consists of sulfite linkages $\{O-\overset{\overset{\displaystyle O}{\|}}{S}-O\}$. The monomer distribution depends on the particular catalyst employed. Polymers prepared with $SnCl_4$ or $SbCl_5$ as the catalyst show long-range order over runs of propylene oxide as long as twelve, and show a strong non-Markoffian dependence on charge ratio, i.e. the ratio of the two monomers present. The catalyst Et_2Zn produces a monomer distribution having no long-range order and having weak Markoffian dependence on charge ratio[134].
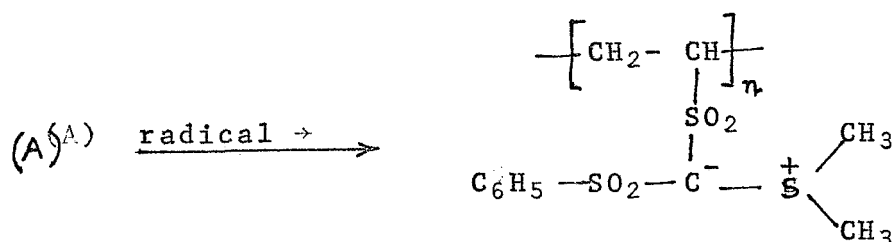
A few other novel polymers bearing sulfony groups in the repeating units.

Diefenbach and coworkers[135] recently reported methods of preparation and polymerization of two S-vinyl sulfonyl ylids, dimethylsulfoniophenylsulfonyl (vinylsulfonyl) methanide (A) and triphenylphosphoniophenyl sulfonyl (vinyl sulfonyl) methanide (B):

<div align="center">(A)   (B)</div>

(A) was readily polymerized in dioxane and dimethyl formamide solutions and both (A) and (B) were copolymerized with styrene

in dienethyl formamide solution using azobisisobutyronitrile
as the initiator. The structure of the homopolymer of (A)
may be represented as:

$$(A) \quad \underline{\text{radical}} \rightarrow \quad \begin{array}{c} -\left[CH_2- \underset{|}{CH}\right]_n- \\ SO_2 \\ | \\ C_6H_5 -SO_2-C^- \underset{}{\overset{+}{S}} \Big\langle \begin{array}{c} CH_3 \\ CH_3 \end{array} \end{array}$$

Goethals[136] studied the polymerization of alkyl vinyl
sulfonate, $CH_2=CH-SO_2O-CH_2CH=CH_2$, and observed that this
briunsaturated compound presents an interesting case where
the two double bonds have significantly different reactivities.
Linear soluble polymers were obtained by solution polymeri-
zation with a radical initiator, but polymerization in the
absence of solvents resulted in insoluble polymers. This
solubility characteristic of the polymers obtained under var-
ious conditions and the determination of their olefenic unsat-
uration indicated that poly (alkyl vinyl sulfonate) contains
a significant amount of six-membered sultone rings:

sultone

etc.
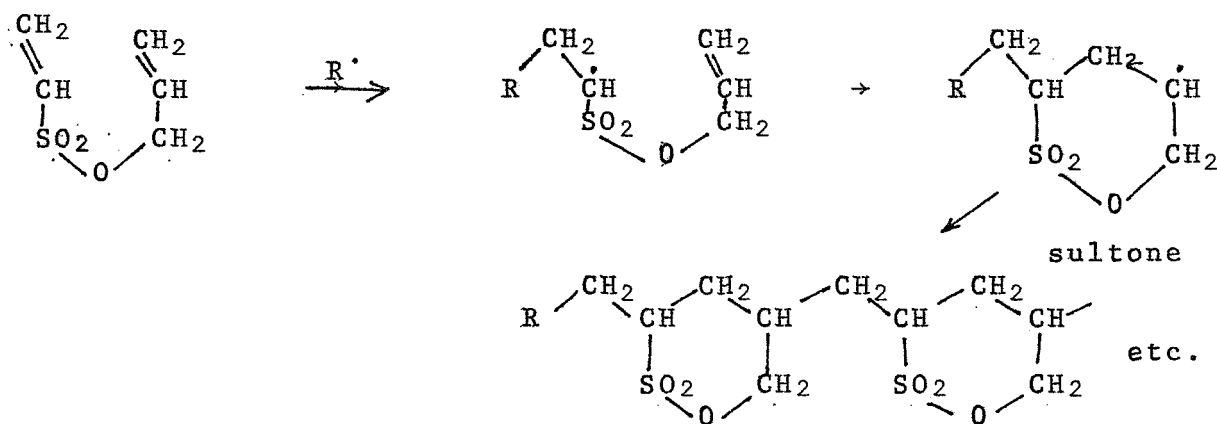
The mechanism of sultone ring formation involves alternating inframolecular-intermolecular chain propagation as shown above.

Polymerization of some fluorothiocarbonyl compounds

Addition polymerization of some interesting non-vinyl sulfur compounds (fluorinated) has recently been described by Sharkey[137], viz., the polymerization of thiocarbonyl fluoride $CF_2=S$ and other fluorothiocarbonyl compounds. Thiocarbonyl fluoride undergoes polymerization readily at low temperatures[138]. The addition of a trace of a very mild base, e.g. dimethyl formamide, to a solution of $CF_2=S$ in dry ether at $-78^{\circ}c$ starts a fast reaction giving rise to polymers of very high degree of polymerization. The structure of the polymer is believed to be $CF_3-S(CF_2S)_n CF=S$. The polymer is a highly resilient elastomer in the amorphous form, but suffers the disadvantage of slow crystallization at temperatures below $35^{\circ}c$, while above $175^{\circ}c$ it depolymerizes. Fluorothioacyl fluorides, such as $CF_3 \cdot CF=S$, $ClCF_2 \cdot CF=S$ and $HCFCL \cdot CF=S$ also undergo anionic polymerization to give elastomeric products. Hexafluoro thioacetone $CF_3- \overset{\overset{S}{\|}}{C} - CF_3$ polymerizes at $-110^{\circ}c$ to give a white elastomeric product that gradually depolymerizes at room temperature to regenerate the monomer. Interestingly, the thiocarbonylfluoride, $CF_2=S$ is found to be susceptible to free radical polymerization at very low temperatures[139]. A redox system of trialkyl boron

and oxygen has been used at -78°c to give high polymers of $CF_2=S$ in bulk or in solution. The radical-generation step for this redox system is described as follows:

$$R_3B + O_2 \rightarrow R_2BOOR \xrightarrow{2R_3^!B} R_2BOBR_2^! + R_2^!BOR + 2R'\cdot$$
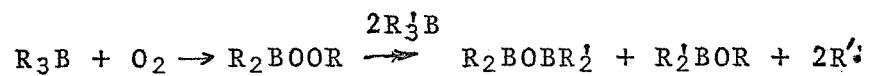
A variety of copolymers of vinyl compounds and $CF_2=S$ may be prepared by using this initiator system.

Acknowledgement

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